BC Environment

A REVIEW OF THE ENVIRONMENTAL IMPACT AND TOXIC EFFECTS OF TCMTB

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SUMMARY

The purpose of this paper is to review the toxicological, environmental, and physical properties of TCMTB, an effective agent in preventing sapstain and fungus growth in freshly cut timber. Two products containing TCMTB, Busan 1030, and Busan 30WB, are also evaluated in terms of their environmental and toxicological impacts.

Several environmental fate studies have been done on TCMTB, but effects of its environmental degradation products have not been fully documented. A partial aquatic degradation pathway has been proposed, and includes hydrolysis and photolysis of TCMTB to various benzothiazoles. Hydrolysis of TCMTB is accelerated at high pH, and is affected by salinity and ion strength. Photolysis also occurs. TCMTB is rapidly degraded under aerobic conditions, and moderately so under anaerobic conditions. Bacterial metabolism has also been shown to occur.

TCMTB has a high affinity for organic material in soil, and its mobility in soils varies according to organic content. It is not mobile in concrete, but is extremely so in asphalt. TCMTB leaches from wood; increasing storage time after treatment decreases the amount leached.

In rats, TCMTB is rapidly absorbed from the intestinal tract after oral dosing, and is distributed in low levels to fat and other tissues. It is excreted mainly via the urine, and is apparently completely metabolised to conjugated products. According to the toxicity scales used in this paper, TCMTB is moderately toxic to mammals orally and dermally, and extremely toxic to several species of fish. Toxic effects in fish appear to be increased in saltwater.

Long term animal testing indicates that TCMTB is unlikely carcinogenic. Mutagenicity tests have also generally given negative results. TCMTB has not been shown to be teratogenic or fetotoxic. Dermal contact is the main route of occupational exposure; possible effects include skin rashes, inflammation, or burns. Eye, nose, and throat irritation, chest tightness, and nosebleeds have also been reported.

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1.0 INTRODUCTION

Large volumes of chlorophenol compounds have previously been used in Canada to preserve and protect wood from attack by various pests. Concerns about acute aquatic toxicity, occupational impacts, and presence of hazardous impurities and breakdown products, including dioxins and furans, in chlorophenols are among the reasons for dissatisfaction with their use (1). The Canadian Lumber Industry has thus phased out the use of chlorinated phenols for sapstain control, and the use of alternative chemicals has increased. Currently there are several pesticides registered by Agriculture Canada which may be used for the protection of freshly cut lumber. These antisapstain materials may contain one or more of the following "active" ingredients: 2-(thiocyanomethylthio)benzothiazole (TCMTB), 3-iodo-2-propynyl butyl carbamate (IPBC), didecyldimethylammonium chloride (DDAC), sodium carbonate, sodium borate, azaconazole, and copper-8-quinolinolate (Cu-8).

The purpose of this paper is to review the environmental and toxicological properties of TCMTB, Busan 1030, and Busan 30WB. TCMTB is the active ingredient in Busan 1030 and Busan 30WB, which are antisapstain products produced by Buckman Laboratories for the wood protection industry. A critical evaluation of their toxicological and environmental impacts has been assisted by Buckman Laboratories' cooperation in providing access to full research reports created for various regulatory agencies. Because very little information is available in the scientific, technical, and medical literature on these products, this paper is based largely on the studies received from Buckman Laboratories. Appendix A contains a list of databases searched for information on TCMTB.

2.0 HISTORICAL BACKGROUND AND USES

The commercial use of TCMTB apparently originated in Buckman Laboratories, Inc. of Memphis, Tennessee (2). In the late 1940's, this company became involved in the search for solutions to the problem of breaks in paper on high speed paper machines due to the formation of microbiological slime. The company first developed the microbicide BSM-11, a product containing mercuric acetate and trichlorophenol, which seemed to find acceptance in the paper making industry.

However, in view of the potential for adverse health and environmental impacts from the use of mercury compounds, Buckman Laboratories developed a line of organosulphur compounds which also proved to be effective slime control agents. TCMTB is one such compound, and is a broad spectrum, substantive fungicide that has proved effective in many industries, including sapstain control.

TCMTB was first registered in Canada as a seed treatment in Co-op San Liquid Seed Treatment, which contained 30% TCMTB (3). The registered uses included control of stinking smut or bunt of wheat, and other seed and soil-borne

seed diseases. It has been shown effective as an anti-fungicide in seed (4-6), pulp (7), and cellulose (7) treatment, and as a miticide (8). One of the more interesting potential applications is the use of TCMTB as a chemotherapeutic agent in the treatment of histoplasmosis (9), a disease characterized by influenza-like symptoms and pneumonia, and caused by the soil-borne organism *Histoplasma capsulatum*. More recently, results of laboratory and field trials have shown that TCMTB has excellent potential as a molluscicide (10).

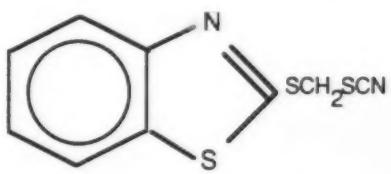
TCMTB was registered in 1977 as an agent to resist mould and sapstain on freshly cut lumber (11). In September 1986, the first Canadian sawmill converted to TCMTB. Two products, Busan 1030 and Busan 30WB, are now registered pesticides with Agriculture Canada (13,14). Busan 1030 is a 30% TCMTB solvent-based formulation and Busan 30WB is a 30% TCMTB water-based formulation (15). Under license with Buckman Laboratories, several companies in B.C. have in the past made 30% TCMTB formulations available for the purpose of sapstain control. Brand names include Woodblok 30 (16), Diachem Woodstat (17), and Concentrate B30 T1090 Liquid Microbiocide (18).

Busan 1030 is recommended for a host of other applications including the control of microorganisms in cooling water systems, wooden cooling towers, water-thinned cutting fluids, crude and refined oils, drilling fluids, and paints (19, 20).

Because of a hydrocarbon solvent odour associated with Busan 1030 and a cold stability problem with Busan 30WB, a new 30% TCMTB low odour, solvent-based modified formula, designated Busan 1118, has been developed by Buckman. This new product will be introduced upon completion of Agriculture Canada registration procedures (15, 21).

3.0 PHYSICAL AND CHEMICAL PROPERTIES

The structural formula of TCMTB is shown below:



(CAS Registry No.: 21564-17-0)

TCMTB is a viscous reddish liquid with a slight odour. It is soluble in organic solvents such as acetone, dimethylformamide, cyclohexanone, benzene, and xylene (3). Solubility in water has been measured at 40 mg/L (24°C, pH 6.5), (116), 16 mg/L (5°C, pH 6.5) (116), and 15 mg/L (5°C, pH 8.5) (116). TCMTB has a specific gravity of 1.38 (3), a boiling point greater than 120°C (3), and a vapour pressure of 3.6×10^{-6} torr (23). The octanol/water partitioning coefficient has been

reported to be 25 (log Kow = 1.40) (22). Log Kow's of 3.12 (24°C), and 3.15 (24°C and pHs of 6.5 and 8.5) have also been recorded (116).

Chloromethylthiocyanate (CMTC) and 2-mercaptobenzothiazole (2-MBT) are stated in one report as the two major starting chemicals used to manufacture TCMTB (24), but confidential data obtained from Buckman Laboratories indicates another preparative method may now be used.

TCMTB is sold commercially as 80% technical material under the trade name "TCMTB" by Buckman Laboratories, which is the sole manufacturer of the material (16, 25). The supplier normally mixes TCMTB with solvents to form a concentrate. Emulsifiers or surfactants may be added to the concentrate to improve the stability of emulsions formed when the concentrate is diluted with water (16).

Busan 1030 is a chemically stable, dark brown liquid composed of 38% technical grade TCMTB, 25% organic glycol ether solvent, 23% aromatic hydrocarbon solvent, and 13% sulfonate/non-ionic surfactant blends (18). Normally diluted to a 0.5-4% solution depending on use, it may be applied to freshly cut lumber through spraying or dipping systems (15). Busan 1030 has a specific gravity of 1.08, a flash point of 50°C, and a characteristic odour. It is miscible with water, and has a pH of 6-7 at 100 ppm in water. Its boiling point is unknown and there are no known chemical incompatibilities.

Busan 30WB is a milky white liquid composed of 38% technical grade TCMTB, 15% fatty acid amine derivatives, 14% organoethoxylate, 7% other organics, and 25% water (18). It is diluted to a 2-4% solution, depending on use, and applied in the same manner as Busan 1030 (15). Busan 30WB has a specific gravity of 1.11, a flash point and boiling point greater than 100°C, a slight odour, and a pH of 4-5. It is also dispersible in water, with a pH of 5-6 at 100 ppm in water. There are no known chemical incompatibilities. Like Busan 1030, various surfactants and emulsifiers are used to keep the TCMTB in suspension.

3.1 By-Products

According to a report from the manufacturer, TCMTB slowly hydrolyzes in water to produce 2-MBT, with the release of small amounts of hydrogen sulfide and formaldehyde (28, 114). 2-MBT may also be present in solution as a by-product of the manufacturing process. However, analyses of Woodblok 30 (a formulation of TCMTB) and its spray solution showed that 2-MBT, and BT, were not present in the samples at the limit of detection (20 ppb) (28).

Information released from Buckman Laboratories (22) states that CMTC is an unavoidable impurity in the final product, and that hydrogen cyanide may be released from TCMTB.

3.2 Thermal Decomposition Properties

Concentrates of TCMTB are flammable (15). Decomposition products during a fire would include hydrogen cyanide, sulphur oxides, benzothiazoles, and nitrogen oxides, which could pose serious environmental and health hazards (15, 29).

Combustion of TCMTB at 500°C results in 99% destruction of the compound, with the possible formation of the compounds mentioned above. Combustion in an efficient hog fuel boiler at 880°C will result in the complete destruction of TCMTB if provisions are made to remove sulphur dioxide from the stack effluent (29).

Busan 1030 is slightly more stable than technical grade TCMTB. The TCMTB portion is destroyed at 600°C, and combustion is complete at 980°C. Several other combustion products have been noted in addition to those already listed for pure TCMTB. These include chloromethyl-thio-benzothiazole, C4-benzene, polyethyl ether, naphthalene, and toluene (30).

4.0 ENVIRONMENTAL SOURCES, DISTRIBUTION, AND BEHAVIOUR

TCMTB is unlikely a naturally occurring material. Its sources in the environment would include spills and other unintentional discharges, permitted discharges from commercial facilities using the substance, as well as discharges from certain materials such as leather, wood, paper, paint, and seeds (1). No reports of measurements of environmental levels of TCMTB were located.

The environmental behaviour of TCMTB has been investigated in a variety of experiments. A series of detailed reports (31-37) addressing environmental behaviour of TCMTB and designed to meet the requirements of the Pesticide Assessment Guidelines of the United States Environmental Protection Agency were completed in 1987. The results of these studies are summarized below. All studies failed to find significant levels of volatile TCMTB degradation products. Where available, information from other sources is also included.

4.1 Aqueous Hydrolysis

The first study (31) considered the hydrolysis of carbon-14 labelled TCMTB at 10 ppm in aqueous solutions buffered to pH 5, 7, and 9. The solutions were kept in the dark and analyzed by thin-layer chromatography at specified time intervals ranging from 0-35 days for pH 5 and 7 samples, and from 0-122 hours for pH 9 samples.

TCMTB was stable at pH 5. It slowly degraded at pH 7, with 8% hydrolyzed after 35 days. At pH 9, the hydrolysis was much more rapid, with a half life of 81 hours, and approximately 70% degradation over 120 hours. 2-MBT is apparently the major hydrolysis product of TCMTB (27), but other unspecified hydrolytic products were observed at this pH, representing 43% and 18% of the TCMTB after 122 hours.

Preliminary research on hydrolysis of TCMTB in various buffering systems found shorter half-lives of TCMTB in Tris buffer versus borax-phosphate buffer (116). Half-lives were dependent on pH (e.g. 1/20 borax-phosphate at 24°C and pH 7.0 had a half-life of 8330 hours; at pH 9.0, $T_{1/2}$ was 83 hours), and on temperature: 1/20 borax-phosphate at pH 8.0 and 15°C had a half-life of 4360 hours; at 5°C, $T_{1/2}$ was 18500 hours (116).

Ongoing research on TCMTB breakdown (27) indicates that the hydrolysis of TCMTB is affected by salinity and ion strength. Both specific and general base catalysis could thus be important reactions affecting the fate of TCMTB in surface waters (116). Studies on the effect of salinity on the half-life of TCMTB involved following degradation of the compound in West Vancouver well water, Fraser River water, and Georgia Strait seawater (27, 116). Half-lives were 1250 hours, 2710 hours, and 740 hours, respectively.

4.2 Artificial and Natural Sunlight Degradation on Soil

The fate of TCMTB on soil was studied (32) by spiking Fox sandy loam soil with approximately 10 ppm carbon-14 labelled TCMTB in petri dishes and following its behaviour in darkness, under continuous artificial sunlight using two Chroma 50 lamps, and under natural sunlight. The samples were maintained at 25°C. Following treatment, the radioactivity distributions of the soil extracts were determined by thin-layer chromatography.

Assuming first order kinetics, the half lives were calculated as follows:

	T 1/2 Artificial Sunlight	T 1/2 Natural Sunlight
Experimental	388 hours	23 hours
Control	917 hours	662 hours

From the table above, it is evident that thermal degradation occurred in the control samples, and that it is enhanced by both types of radiation. Degradation products were not identified. In the absence of other evidence, the extreme differences in half-lives for the two experimental conditions suggests that artificial sunlight is not a good substitute for natural sunlight.

4.3 Artificial Sunlight Degradation in Aqueous Solution

The photodegradation of carbon-14 labelled TCMTB was followed by the irradiation of 10 ppm solutions of TCMTB in sterilized sodium acetate pH 5 buffer at 25°C (33). Chroma 50 lamps, which were said to have spectral distributions similar to that of natural sunlight, were used as the radiation source. The degradation appeared to follow first-order kinetics, with a half-life of 3.8 hours. After 8 hours, 28% of the TCMTB remained. No degradation was noted in control samples, which were wrapped in metal foil but otherwise subjected to the same experimental conditions. The major degradation product was tentatively identified as 2-MBT.

Further research on photodegradation of TCMTB in dilute potassium phosphate buffer (pH 6) found that TCMTB breaks down rapidly by direct photolysis, giving 2-MBT as the major product (~50% yield) and traces of BT as a minor product (116). An estimation of rates of photodegradation in natural systems gave estimated half-lives for both TCMTB and 2-MBT on the order of one day or less for dilute solutions in surface waters and full sunlight, even in the presence of moderate concentrations of dissolved organic matter (DOM) (116).

4.4 Aerobic Aquatic Metabolism

An experiment using carbon-14 labelled TCMTB studied the aquatic metabolism in lake sediment and water (34). The lake sediment, collected from Lake Mendota in Wisconsin, had 96% sand, 3% clay, and 1% organic matter, with a pH of 7. The lake water had a pH of 8 to 8.5. Spiked samples containing approximately 11 ppm TCMTB were incubated in the dark at 26°C and followed up to 31 days.

The level of TCMTB fell from 88% at day 0 to 1% at day 14, with a calculated half-life of 2.8 days. While six different by-products were observed, only two were tentatively identified. A compound thought to be 2-MBT increased from 1.4% at day 1 to 10% at day 4, and then decreased to 1% by day 31. Another product, tentatively identified as 2,2-dithiobisbenzothiazole, increased from 4% at day 1 to a maximum of 14% at day 14, and then declined to nondetectable levels by day 31.

It is interesting to compare the half-life of 81 hours determined from the aqueous hydrolysis study above at pH 9 (31), with the half-life in the sediment and water, which is about 67 hours. Since the rate of hydrolysis is less at lower pH values, and since the pH of the sediment and water is slightly less than 9, one might expect a water/sediment half-life above 81 hours to result solely from non-biological degradation mechanisms. Since the experimental result is less than 81 hours, biological degradation mechanisms may be in operation.

4.5 Anaerobic Aquatic Metabolism

One study (15) to determine the fate of TCMTB under anaerobic environmental conditions found a half-life of 4 to 7 days for TCMTB in lake sediment. Complete details of the study were not available, but the major product of metabolism was probably 2-MBT. It appears that 2-MBT is slowly degraded under these conditions to one or more water-soluble compounds.

4.6 Aerobic Soil Metabolism

In this experiment, Dickenson sandy loam soil (15) was fortified with radiolabelled TCMTB at 9.5 ppb and incubated in the dark at 25°C for more than one year. At various times, samples were extracted with acetonitrile:water (4:1), and the extracts partitioned with dichloromethane. The radioactivity in the organic and aqueous phases of the extract, extracted soil, and trapping media

was quantified by liquid scintillation counting, and radioactivity distributions of the extract were analyzed by thin-layer chromatography.

Results showed that TCMTB was rapidly degraded under these conditions, and that the half-life of TCMTB was between 0 and 2 days. By the end of the experiment most of the degradation products were soil-bound, and some of the TCMTB was degraded to carbon dioxide. 2-MBT was only a minor portion of the degradation products but the actual amount was not specified. It was also degraded.

4.7 Bacterial Metabolism

To determine whether TCMTB is metabolised by bacteria (35), the following solutions were incubated for a period of three days with a mixed culture of bacteria: 1) a 10 ppm solution of TCMTB, 2) a 10 ppm solution of TCMTB containing glucose and ammonium ion, and 3) a 10 ppm solution of TCMTB containing glucose and nutrient broth. At the end of the incubation period, the solutions were extracted with methylene chloride and the extracts analysed for TCMTB. Growth was observed only in the flask containing nutrient broth, and the extract showed no TCMTB. Essentially 100 percent of the TCMTB was recovered from the other two flasks, indicating that metabolic breakdown of TCMTB occurred only when glucose and nutrients were available.

Research on 2-MBT incubated in the presence of a suspended sediment showed conversion to 2-(methylthio)benzothiazole (MTBT) in low yield, probably by biologically-mediated methylation of the mercapto group (116). A quantitative assessment of the reaction was not done.

4.8 Effects on Soil Components

Dacre (38), in his preliminary toxicological evaluation of TCMTB and other potential replacements for chlorophenates, noted a study (39) on the impact of soil treatment with TCMTB (50-300 ppm). The composition of the soil microflora was changed by the replacement of *Fusarium*, *Penicillium*, *Aspergillus*, *Trichoderma*, and *Chaetomium* species with *Streptomyces*. Soil urease enzyme activity and the ammonifying capacity of the soil were also inhibited.

4.9 Adsorption/Desorption on Agricultural Soils

In this experiment (36), Plainsfield sand, Plano silt loam, Fox sandy loam, and Kewaunee clay loam were each equilibrated with aqueous solutions of carbon-14 labelled TCMTB of 0.5, 1, 5, and 10 ppm at 25°C for 2 hours. While all the soils adsorbed the TCMTB to some extent, the equilibrium constants varied from 1.9 for the Plainsfield sand, which is low in organic matter (0.8%), to 38.4 for the Kewaunee clay loam (2% organic matter). The results indicate that the higher the proportion of organic material in the soil, the greater affinity TCMTB has for it and the greater potential it has for removing TCMTB from water. A subsequent desorption test showed a range of 2.9% to 28.8% removed from the soil after 2 hours.

4.10 Mobility on Soils

The mobility of carbon-14 labelled TCMTB on four soils was studied (37) by coating glass plates with thin layers of soil, spotting the plate with TCMTB, and 2,4-D and Paraquat (as reference standards), and then allowing water to migrate up the plates. Consideration of the distance the spots moved suggested that TCMTB should be classified, using USEPA mobility classes, as "mobile" in the Plainsfield sand and as having "low mobility" in the Mississippi silt loam, Fox sandy loam, and Hagerstown silty clay loam.

The mobility of soil-aged TCMTB residues has also been investigated (41). Dickenson sandy loam was fortified with 9.5 ppm of carbon-14 labelled TCMTB and incubated at 25°C for 32 days under dark, aerobic conditions. A sample of the aged soil was subjected to thin-layer chromatography and eluted with water. The soil-aged TCMTB residues were more mobile than nonsoil-aged TCMTB residues. The soil-aged residues were classed as "mobile", while the nonsoil-aged residues were labelled "low mobility".

4.11 Mobility in Concrete and Asphalt

An assessment of penetration of TCMTB into concrete and asphalt areas was located (42). In this study, concrete, asphalt, and soil core samples were taken at the Fraser Surrey Docks and tested for TCMTB by high performance liquid chromatography (HPLC). Results indicated that TCMTB does not penetrate concrete, but instead seems to be broken down under the alkaline conditions of the concrete. The concentrations of TCMTB on the concrete surface ranged from 9 ppm to 70 ppm. Soil samples taken below the concrete layer did contain some TCMTB (<0.3 ppm), but this may have been due to cross-contamination from the coring bit.

Results from asphalt samples showed that TCMTB penetrates asphalt, and contaminates the soil below the asphalt. Surface concentrations of TCMTB ranged from 37 ppm to 398 ppm, while soil below the asphalt contained from 0.6 to 197 ppm TCMTB. An asphalt sealing compound of unknown constitution did not prevent TCMTB penetration.

4.12 Leaching and Effluent Behaviour

Four studies on leaching of TCMTB from treated lumber were found. The first study (43) was conducted to determine the quantity of TCMTB leached from freshly dip-treated lumber exposed to rain. A simulated rainfall of 20 mm in 6 hours was used to determine the quantity of chemical leached from packaged lumber for 1, 3, and 24 hour delay periods after treatment.

The data obtained showed less TCMTB leached from samples tested 1 to 3 hours after treatment application than the amount of chlorophenol leached in similar tests on chlorophenate dipped lumber (44). However, TCMTB leaching was 1.5 to 2 times higher than the levels found with chlorophenate spray treated

lumber evaluated in an earlier study (45). The amount of TCMTB leached dropped by 50% with a 24 hour delay between treatment and leaching, indicating partial fixation of the TCMTB to the wood surface.

The objective of the second study (40) was to determine the range of TCMTB levels in rainwater draining off or through unprotected packages of lumber dip-treated with Busan 1030. Packages of lumber were treated with 25 ug/cm^2 of TCMTB, stored for 12 to 24 hours, then set out individually in the lumber yard and exposed to rain. Rainwater leachate was collected in jars placed beneath the packages, and samples were analysed by HPLC using a reverse phase column and a variable wavelength detector.

Leachate containing between 570 and 7200 ppb of TCMTB was found running off dip-treated packages exposed to rainfall of 42 mm over 10 days. Approximately 1.5% of the TCMTB retained on the wood was estimated to leach off during the period of treatment. However, this would be an overestimate of the amount leached because it is based on the assumption that all the rain falling on the package washes through the lumber and into the environment.

The third study (46) estimated the concentration of TCMTB in stormwater runoff from treated lumber storage yards which apply the minimum 2.5 hours of covered storage after treatment, as outlined in the BC Provincial Government Code of Good Practice. Using a comparative study of TCMTB and chlorophenol leaching rates, it was concluded that leachate at the storm drain would have a concentration ranging from 142 ppb to 513 ppb. This value is based on a composite sample in which aliquots were collected every 15 minutes for a 3 hour period during a continuous storm event.

The fourth study (47) investigated concentrations of TCMTB and its degradation products in rainwater leachate from surface treated lumber, and in the Fraser River adjacent to stormwater outfalls which drain lumber storage yards. Samples of rainwater were collected directly from dripping lumber after high pressure spray treatment, and from discharges from the storage yard. Fraser River water samples were collected at various locations and depths adjacent to the discharge during periods of rainfall. All samples were analysed by HPLC for the presence of TCMTB, 2-(methylthio)benzothiazole (MTBT), 2-MBT, and BT.

Results show that lumber which had less than one hour of covered storage leached at an average concentration of 89,000 ppb TCMTB, <25 ppb 2-MBT, <20 ppb BT, and 1000 ppb MTBT. Yard runoff to the storm sewer averaged concentrations of 7500 ppb TCMTB, 1155 ppb 2-MBT, <20 ppb BT, and 63 ppb MTBT. When allowed 12 to 24 hours of covered storage, the TCMTB concentration in leachate fell by 94% in comparison to lumber stored for less than one hour. Treated lumber stored for greater than 12 to 24 hours leached at an average concentration of 5433 ppb TCMTB, 1500-2000 ppb 2-MBT, 110-385 ppb BT, and 32 ppb MTBT. Discharges to sewer averaged 340 ppb TCMTB, <25 ppb 2-MBT, <25 ppb BT, and 15-27 ppb MTBT. The optimum covered storage time for all treatment methods (dip treatment, and low and high pressure spray) was estimated to be four hours.

The study also indicated that the effluent plume discharged from a sawmill in the lower Fraser River will stratify in the top metre of the river, regardless of the tidal cycle, creating an acutely toxic zone extending ten metres from the discharge on at least 30 days per year and 10 to 20 metres on at least five days per year. It was estimated that within these distances, the plumes will remain acutely toxic for five to ten hours, or for as long as rainfall continues.

The measured levels of TCMTB in leachate and effluent in these studies should be compared to existing regulations for antisapstain chemicals (48), which stipulate that the concentration of TCMTB in effluent shall not exceed 15 ppb. Evidently, a large discrepancy exists between allowable levels and actual measured levels of TCMTB in these mill discharges.

4.13 Environmental Fate Pathway

A partial pathway for the environmental fate of TCMTB and 2-MBT has been proposed (116), and is summarized below. Hydrolysis and/or photolysis of TCMTB yields 2-MBT, which can then be photolyzed to BT or HOBT, or can undergo biomethylation to MTBT (116). Predicted stable products from TCMTB and 2-MBT degradation include BT, HOBT, and MTBT, all of which have been reported in aquatic systems. Under conditions of chlorine use (e.g. drinking water or sewage disinfection), BT and MTBT may respectively undergo oxidation by hypochlorite to HOBT, and to 2-(methylsulfinyl)benzothiazole (MSiBT) and 2-(methylsulfonyl)benzothiazole (MSoBT). Transformation of the sulfenamides of 2-MBT into 2-MBT has also been proposed (117). 2-MBT may then be photolyzed to BT.

5.0 PHARMACOKINETICS

5.1 Biological Absorption, Transport, and Distribution

Indirect information was located on the absorption and accumulation of Busan 1030, 30WB, or TCMTB by biota. Since these materials are toxic orally and dermally, they are evidently absorbed (1). However, the octanol-water partition coefficient of 25 for TCMTB (22) indicates that bioaccumulation is unlikely.

A rat metabolism study (49) also provides some information. TCMTB fed to rats quickly appeared in the bloodstream, and was subsequently distributed in low levels to the fat and other tissues. Peak plasma radioactivity levels occurred about 0.5 hours after single dose administration, and highest levels in the rat were observed in blood cells. Levels in fat, plasma, and carcass remained relatively low, although some accumulation was observed. Multiple dose experiments after 14 days indicated that some radioactivity accumulated in tissues, but these levels decreased after the final dose. The half-life in blood cells was calculated to be 7 days, and detectable levels of radioactivity were observed in tissues up to 14 days after the administration of the last dose.

5.2 Metabolism and Excretion

One study on the metabolism and excretion of TCMTB was located (49). Using carbon-14 labelled material, Sprague-Dawley rats were fed TCMTB in corn oil by gavage at doses of 3 and 30 mg/kg (single dose) and 3 mg/kg (multiple doses). Generally, only low levels of radioactivity were detected in tissues 4 days after administration. About 80% of the original radioactivity was recovered in urine, about 5% in feces, and the remainder in cage-wash liquid.

Chromatography of radiolabelled components in urine suggested complete metabolism of TCMTB. Results from reaction with ß-glucuronidase showed that the metabolism by-products are likely conjugated.

5.3 Placental and Milk Transfer

No information on placental or milk transfer of TCMTB was located.

6.0 TOXICOLOGICAL EFFECTS

6.1 General Toxicity

There are few published studies on the toxicity of TCMTB, Busan 1030, or Busan 30WB. Confidential information received from Buckman Laboratories indicates that most of the toxicity studies on TCMTB have been done by private laboratories and that this data was submitted to government agencies as part of the pesticide registration process.

The general mammalian toxicity data available on TCMTB, Busan 1030, and Busan 30WB come mainly from Buckman Laboratories and are summarized below. Toxicity ratings are included after each oral, dermal, and inhalation toxicity value and reference, according to the table in Appendix B.

6.2 Mammalian Tests on Technical Grade (80%) TCMTB

			Toxicity
a) Acute Oral LD50 :			
	Rats	~1200 mg/kg (3).	(3)
	Rats	750 mg/kg (26)	(3)
	Rats	2665 mg/kg (males) (51)	(3)
	Rats	2538 mg/kg (females) (51)	(3)
b) Acute Dermal LD50:	Rabbits	~10,000 mg/kg (50,51)	(2)
	Rabbits	>2000 mg/kg (52)	(3)
	Mice	556 mg/kg (males) (55)	(3)
	Mice	702 mg/kg (females) (55)	(3)
	Rats	> 2000 mg/kg (53)	(3)
	Rats	1590 mg/kg (60% form) (54)	(3)

			Toxicity
c) Inhalation LC50 (4 hr):	Rats	0.0802 mg/L (males) (98)	(5)
	Rats	0.131 mg/L (males) (26)	(5)
	Rats	<0.06 mg/L (females) (98)	(5)
	Rats	0.139 mg/L (females) (26)	(5)
	Rats	0.0671 mg/L (combined) (98)	(5)
	Rats	0.135 mg/L (combined) (26)	(5)

d) Primary Eye Irritation:

Rabbits corrosive (26)

e) Primary Skin Irritation:

Skin irritation tests using rabbits indicate that TCMTB is a severe skin irritant (26). Irritation in guinea pigs has also been reported at TCMTB concentrations of 10% and higher (22).

f) Dermal Sensitization:

Guinea Pigs strong sensitizer (55)

g) Feeding Studies

90 Day Feeding Study - Mice (58): In a dose range-finding study for a 104 week oncogenicity study (Section 7.0), groups of 10 male and 10 female CD-1 mice received 0, 10, 30, 70, and 100 mg TCMTB/kg/day in the diet for 13 weeks. After dosing, all mice were killed and necropsied; histopathological examination was conducted on selected organs.

Reduced food consumption was noted in both sexes at 100 mg/kg/day and in males at 70 mg/kg/day. No other signs of toxicity were observed.

90 Day Feeding Study - Rats (58): A dose range-finding study for a 104 week chronic toxicity/carcinogenicity study (Section 7.0) involved dietary administration of 0, 10, 30, 70, and 100 mg TCMTB/kg to groups of 10 male and 10 female Sprague-Dawley rats. After dosing for 13 weeks, all rats were killed and and underwent necropsy. Histopathological examination of the liver, heart, kidneys, lungs, and spleen was also carried out on all animals in the control and high dose groups. Stomachs were examined from selected animals in the control, low, intermediate, and high dose groups.

Results showed a reduced body weight gain in both sexes at 70 and 100 mg/kg/day, reduced food consumption in both sexes at 100 mg/kg/day, and in males at 70 mg/kg/day. At dose levels of 30 mg/kg/day and above, squamous epithelial hyperplasia of the stomach was evident. There were no effects observed at 10 mg/kg/day.

90 Day Feeding Study - Rats (25): No treatment-related changes were noted in body weight, food consumption, hematology, clinical chemistry, urinalyses, and organ weights at doses of 333, 500, and 750 ppm. Treatment-related effects noted at necropsy included inflammation, edema, and degenerative lesions with necrosis of squamous epithelium and ulceration of the non-glandular stomach mucosa at 750 ppm in males. Mild inflammatory changes were observed in several male rats at 750 ppm and in a few female rats at 500 ppm. The No Observed Effect Level (NOEL) for this study was set at 333 ppm, or about 14 mg TCMTB/kg/day.

90 Day Feeding Study - Beagle Dogs (25): No treatment-related changes were observed at 20, 150, or 500 ppm dietary levels. The animals were examined for changes in body weight, food consumption, behaviour, blood cell counts, blood and urinalyses, weight, and appearance of organs and tissues. The NOEL for this study was set at 500 ppm or about 12.5 mg/kg/day (16).

52-Week Feeding Study - Beagle Dogs (104, 26): Chronic oral administration of TCMTB at dietary concentrations of 100, 300, and 1000 ppm elicited essentially no toxic effects, although the high dose group showed a slight decrease in body weight gains. Clinical signs, body weight, and food consumption were observed throughout the study. As well, laboratory investigations of hematology, clinical chemistry, and urinalysis were undertaken prior to test initiation and during weeks 13, 26, and 52 of treatment. Ocular examinations were done pretrial and during weeks 26 and 51 of treatment. These examinations showed no TCMTB-associated changes. Terminal studies of organ weights, gross pathology, and histopathology also showed no significant treatment-related effects for any dose group. Hematological and clinical chemistry tests were also normal. The NOEL based on body weight gain may be considered to be in the region of 300 ppm TCMTB.

6.3 Mammalian Tests on Busan 1030

			Toxicity
a) Acute Oral LD50:			
	Rats	1200 mg/kg (22)	(3)
	Rats	800 mg/kg (females) (22)	(3)
	Rats	1900 mg/kg (males) (22)	(3)
b) Acute Dermal LD50:			
	Rabbits	1080 mg/kg (57)	(3)
c) Inhalation LC50 (4 hr):			
	Rats	0.26 mg/L (males) (99)	(4)
	Rats	0.10 mg/L (females) (99)	(5)
	Rats	0.20 mg/L (combined) (99)	(5)
d) Primary Eye Irritation:	Rabbits	corrosive (50)	

e) Primary Skin Irritation: Rabbits severely irritating (101)

f) Dermal Sensitization: Guinea Pigs moderate sensitizer (18).

g) Feeding Studies:

No feeding studies were located.

6.4 Mammalian Tests on Busan 30WB

			Toxicity
a) Acute Oral LD50:	Rats	1200 mg/kg (59)	(3)
	Rats	1000 mg/kg (females) (59)	(3)
	Rats	1300 mg/kg (males) (59)	(3)
b) Acute Dermal LD50:	Rabbits	>2000 mg/kg (60)	(3)
c) Inhalation LC50 (4 hr):	Rats	<0.4398 mg/L (100)	(4)
d) Primary Eye Irritation:	Rabbits	corrosive (62)	
e) Primary Skin Irritation:	Rabbits	severely irritating (60)	
f) Dermal Sensitization:	Guinea Pigs	moderate sensitizer (15)	

g) Feeding Studies

No feeding studies were located.

6.5 Aquatic Species Tests on Technical Grade and Pure TCMTB

The following aquatic toxicity studies were performed under either static (s), flowthrough (f), or unspecified (u) conditions. Toxicity ratings follow each value and reference, as outlined in Appendix C.

a) 96 hour LC50:			Toxicity
Corrected to 100%	Rainbow Trout	(s) 0.039 ppm (64)	(5)
	Rainbow Trout	(s) 0.054 ppm (64)	(5)
	Rainbow Trout	(s) 0.045 ppm (64)	(5)
	Chinook Salmon	(s) 0.015 ppm* (55)	(5)
	Chinook Salmon	(s) 0.018 ppm (64)	(5)
	Sheepshead Minnows	(u) 0.036 ppm (63)	(5)
80% TCMTB	Rainbow Trout	(s) 0.050 ppm (65)	(5)
	Rainbow Trout	(s) 0.052 ppm (65)	(5)
	Rainbow Trout	(s) 0.047 ppm (65)	(5)

*Toxicity value used for establishing stormwater effluent legislation (Appendix D).

			Toxicity
80% TCMTB	Rainbow Trout	(f) 0.021 ppm (26)	(5)
	Bluegill Sunfish	(f) 0.0087 ppm (26)	(6)
	Chinook Salmon	(s) 0.026 ppm (65)	(5)
	Chinook Salmon	(s) 0.025 ppm (65)	(5)
	Sheepshead Minnow	(u) 0.060 ppm (26)	(5)
	Shrimp	(u) 0.021 ppm (26)	(5)
60% TCMTB	Rainbow Trout	(u) 0.029 ppm (25)	(5)
	Bluegill Sunfish	(u) 0.047 ppm (25)	(5)
	Harlequin Fish	(u) 0.036 ppm (25)	(5)

b) 48 hour LC50

80% TCMTB	*Daphnia pulex*	(u) 850 ppm (50)
	Daphnia pulex	(u) 0.060 ppm (55)
	Daphnia magna	(f) 0.022 ppm (26)
	Mysid Shrimp	(u) 0.023 ppm (55)
	Mysid Shrimp	(u) 0.021 ppm (26)
	Quahog clam	(u) 0.014 ppm (26)
60 % TCMTB	Rainbow Trout	(u) 0.036 ppm (25)
	Bluegill Sunfish	(u) 0.079 ppm (25)
	Harlequin Fish	(u) 0.075 ppm (25)

c) 24 hour LC50

60% TCMTB	Harlequin Fish	(u) 0.13 ppm (25)

Citations from the Japanese literature were also found for carps, tadpoles, and several other species, but data were not available in the English abstracts.

d) 30 day LC50

80% TCMTB	*Mytilus edulis*	(u) 1.4 ppm (26)

e) Chronic-Exposure Toxicity

No chronic exposure studies were available for review.

f) Saltwater versus Freshwater Studies with Technical Grade TCMTB

Recent preliminary work (66) assessed the effects of TCMTB on salmon at both lethal and sub-lethal levels, using continuous flow bioassays. Coho and Chinook underyearlings, in fresh water and salt water respectively, were exercised by swimming against a current in annular fibreglass channels. Replacement water flows and toxicant were admitted simultaneously and continuously, with ninety percent replacement after 1.5 hours.

Responses to TCMTB included coughing, movement into lower velocity waters, movement to the water surface, gulping, loss of position against water

currents, and, eventually, loss of equilibrium. TCMTB appears to be more toxic in salt water, as shown below. However, such a conclusion must be viewed as tentative due to the different test species, and lack of information on products of hydrolysis in sea water. Further research is now being done to assess physiological and behavioural impacts of TCMTB on fish in artificial and natural conditions (67).

			Toxicity
Freshwater LC50:	Coho Salmon	24hr LC50	0.058 ppm
	Coho Salmon	96hr LC50	0.0176 ppm (5)
	Coho Salmon	168hr LC50	0.0104 ppm
Salt Water LC50:	Chinook Salmon	24hr LC50	0.015 ppm
	Chinook Salmon	96hr LC50	0.0057 ppm (6)
	Chinook Salmon	168hr LC50	0.0042 ppm

g) Bioconcentration and Elimination of TCMTB

One study of ^{14}C-residues in bluegill sunfish exposed to ^{14}C-labelled TCMTB under flowthrough conditions was located (102). Fish were continuously exposed to a nominal concentration of 280 ng/L of ^{14}C-TCMTB in well water for 28 days, after which 35 fish were transferred to flowing, uncontaminated water for a 14-day depuration period. Sampling intervals during the exposure period were days 0, 1, 3, 7, 10, 15, 21, and 28, and during the depuration period were days 1, 3, 7, 10, and 14.

Results showed that bioconcentration potential is low to moderate. The concentration of ^{14}C-residues in the edible, nonedible, and whole body tissues of the fish reached steady states by days 1, 7, and 7, respectively. The mean steady-state bioconcentration factors for these tissues were 76x, 440x, and 230x, respectively. Rapid elimination of ^{14}C-residues from the selected tissue portions of bluegill and consequently on a whole fish basis was observed during the first three days of the depuration period. Half-life of the ^{14}C-residues present in all tissue portions on the last day of exposure occurred between the first and third day of depuration. By day 14 of depuration, ^{14}C-residues present on the last day of exposure in the edible, nonedible, and whole fish tissues had been eliminated by 71%, 80%, and 78%, respectively.

6.6 Aquatic Species Tests on Busan 1030 and Busan 30WB

Environment Canada has carried out a number of fish bioassays on Busan 1030 and Busan 30WB. The values reported below must be multiplied by 0.3 to obtain the aquatic toxicities based on the concentrations of the active ingredient. Toxicity ratings (Appendix C) follow each value and reference.

			Toxicity
a) 96 hour LC50:			
Busan 1030	Rainbow Trout	(s) 0.13 ppm (63)	(4)
	Rainbow Trout	(u) 0.117 ppm (63)	(4)
	Chinook Salmon	(s) 0.055 ppm (22)	(5)
	Chinook Salmon	(s) 0.06 ppm (63)	(5)
	Mytilus edulis	(u) 2.2 ppm (63)	(3)
	Daphnia magna	(u) 0.076 ppm (63)	(5)
b) 96 hour LC50			
Busan 30WB	Rainbow Trout	(s) 0.15 ppm (63)	(4)
	Rainbow Trout	(s) 0.18 ppm (63)	(4)
	Rainbow Trout	(s?) 0.165 ppm (22)	(4)

6.7 Avian Tests on Technical Grade (80%) TCMTB

a) Dietary LC50:	Mallard Ducks	>10,000 ppm (25)
	Mallard Ducks	>5,620 ppm (26)
	Bobwhite Quail	>10,000 ppm (16)
	Bobwhite Quail	>5,620 ppm (26)
b) Acute Oral LD50:	Mallard Ducks	1310 mg/kg (25)
	Bobwhite Quail	661 mg/kg (26)

6.8 Avian Tests on Busan 1030 and Busan 30WB

No results for toxicity tests on Busan 1030 or Busan 30WB were located.

6.9 Insect Tests on Busan 1030

One study on the toxicity of TCMTB to the eastern subterranean termite (*Reticulitermes flavipes*) was located (86). Thirty individuals were placed in vials that contained sand, water, and strips of filter paper treated with 0.1, 1.0, or 5.0% (w/w) TCMTB, for either 24 hours or 7 days. Repellency was confirmed by the absence of feeding on the TCMTB treated papers over 7 days. Although no significant immediate or post-exposure mortality occurred as a result of the 24 hour exposure period, significant mortality during and after the 7 day exposure suggests that prolonged confinement with a treated substrate exposes insects to either contact toxicity or fumigant action despite the behavioural avoidance response.

6.10 Comparative Toxicity

A comparison of toxicities of various antisapstain active ingredients and formulations is shown in Table 1. Technical grade TCMTB is less toxic orally and dermally to test animals than is NP-1, a competing formulation. However, it is more orally toxic than the Copper-8 and Ecobrite III formulations. In terms of aquatic toxicity, TCMTB is one of the most toxic non-chlorophenol antisapstain compounds available, with a 96 hour LC50 of 0.015 ppm for Chinook salmon.

Although still less toxic than pentachlorophenol (PCP), the solvent-based formulation Busan 1030 is more toxic than TCMTB through the dermal route, probably because solvents used in the formulation increase the absorption of TCMTB, and may themselves exert a toxic effect. Busan 1030 is somewhat less toxic to fish than is technical grade TCMTB, but is still one of the more aquatically toxic antisapstain compounds of those listed.

An important area of difference between TCMTB and PCP is that of aquatic toxicity. TCMTB seems to be more toxic to fish species than does PCP, although the solvent formulation is generally the least toxic of the three substances listed.

Toxicity values for the TCMTB breakdown product 2-MBT are also shown in Table 1. The compound appears to be more toxic orally than its parent, but less toxic dermally and aquatically. Although this analysis may portray 2-MBT as a less toxic chemical than TCMTB, other data, including those from feeding studies, and from carcinogenicity, mutagenicity, and teratogenicity studies, should be considered in the assessment of each chemical (106).

7.0 CARCINOGENICITY

Two carcinogenicity studies, both of 104 weeks duration, have been carried out by Buckman Laboratories. Draft study summaries were provided to the Ministry of Environment (26). In the first study, groups of 50 male and 50 female CD-1 mice were dosed with TCMTB at dietary concentrations designed to give 0, 15, 50, and 150 mg/kg/day. The animals were observed weekly for any clinical signs of toxicity and palpable masses. Food consumption and body weights were recorded once each week up to week 13 and every four weeks thereafter. Differential blood smears were taken after weeks 52, 78, and 103. Animals were sacrificed, and detailed gross necropsy and histopathological evaluations were performed.

Results indicate that doses up to 150 mg TCMTB/kg did not produce any overt signs of toxicity. However, animals in the high dose group did exhibit a significant decrease in body weight gain. An increased incidence of focal and diffuse hyperplasia of the duodenal mucosa was observed in the high dose males. There was no evidence of a carcinogenic effect.

The second study involved dosing 70 male and 70 female rats with dietary concentrations of 0, 2, 8, and 20 mg TCMTB/kg/day. The animals were observed daily for any clinical signs of toxicity. Food consumption and body weights were recorded at specified intervals throughout the study. Laboratory investigations of hematology, clinical chemistry, and urinalysis were undertaken prior to test initiation and during study weeks 13, 24, 51, and 104. Differential blood smears were taken after weeks 52, 78, and 103. Animals were sacrificed and detailed gross necropsy and histopathological evaluations were then performed.

Dietary administration of TCMTB for 52 weeks produced equivocal signs of toxicity, indicated by a slight increase in liver weights for high dose females.

After 104 weeks of dosing, animals did not exhibit any overt signs of toxicity. The only notable histological effect was a slight increase in interstitial cell tumours in the mid and high dose males, and hyperplasia in the stomach of the high dose males and females.

It should be noted that one of the primary degradation products in the environmental fate studies, 2-MBT, has been reported (68) to produce evidence of "some carcinogenic activity" in two year gavage studies in F344/N rats, indicated by increased incidences of mononuclear cell leukemia, pancreatic acinar cell adenomas, adrenal gland pheochromocytomas, and preputial gland adenomas or carcinomas. In female B6C3F1 mice, equivocal evidence of carcinogenic activity was obtained, evidenced by increased incidences of hepatocellular adenomas or carcinomas. A toxicological review of 2-MBT has recently been completed by the BC Ministry of Environment (106).

8.0. MUTAGENICITY

Several reports on the mutagenicity of TCMTB are available and generally give negative results, although some positive results are available. In one study (38), TCMTB was claimed to be mutagenic when tested by the *Salmonella typhimurium* system and by a *Bacillus subtilis*. assay. However, a letter from Buckman Laboratories to its field personnel (69) claims that these tests were only positive for *B. subtilis* without activation, and negative in the *Salmonella* assay. Three studies in Japan were claimed to have yielded similar results (69):

Buckman Laboratories subsequently had two *in vitro* mammalian cell studies carried out on TCMTB (69). Both a forward mutation assay and a sister chromatid exchange assay on Chinese hamster ovary cells gave negative results, with or without metabolic activation (26). In 1981, the USEPA stated (62) that TCMTB was a suspected mutagen, and that further testing would be required to assess its mutagenic potential. Further mutagenicity studies from Buckman, including an *in vivo* micronucleus assay in mice (66), an Unscheduled DNA Synthesis (UDS) test in primary rat hepatocytes (72), and a rat bone marrow cytogenetic test, have all given negative results (26).

BC Research has also carried out Ames reverse-mutation bacterial assays (28) using five strains of *S. typhimurium* on Woodblok 30 and a spray solution created by diluting Woodblok 30. Neither solutions were mutagenic in the presence or absence of metabolic activation.

Screening tests by Vanachter and co-workers (71) showed mutations in *Fusarium oxysporum* and *Rhizoctonia solani*. The authors observed cases of decreased sensitivity of test fungi to the presence of TCMTB, and suggested they would develop resistance to TCMTB within a short time.

9.0 TERATOGENICITY AND REPRODUCTIVE EFFECTS

Three investigations of the teratogenicity or reproductive effects of TCMTB were found. In an experiment on rabbits (74), a mixture of TCMTB in corn oil was administered by gavage as a single dose to three groups of 20 artificially inseminated New Zealand white rabbits. Dose levels were 10, 20, and 40 mg/kg, at a dosage volume of 0.5 ml/kg. Dosing was performed daily from gestation day 6 through 19 in both experimental and control groups.

No clinical signs of toxicity were observed in any of the TCMTB treated groups. No treatment-induced deaths or abortions occurred in the low and mid dose groups, but one death was recorded in the high dose group. Mean maternal weight gain and food consumption were affected by the administration of TCMTB at dose levels of 20 and 40 mg/kg. The effect was statistically significant in the high dose group and only slight in the mid dose group. No body weight gain or food consumption differences were noted between the control and the low dose groups.

Intrauterine survival, fetal sex ratios, and fetal weights were not affected by the administration of TCMTB at any dose level used. Fetal developmental variations occurred with similar frequency in control and treatment groups, suggesting that TCMTB is not teratogenic, embryotoxic, or fetotoxic. The NOEL for developmental effects was therefore greater than 40 mg/kg/day. Because maternal toxicity occurred at 20 and 40 mg/kg, and not at 10 mg/kg, the lowest dose was considered a "no-effect" level for maternal toxicity.

A similar study (75) was performed to assess the teratogenic potential of TCMTB in rats. A mixture of TCMTB and corn oil was administered by gavage to groups of 29 mated female rats at levels of 25.1, 76.5, and 125.5 mg/kg TCMTB from day 6 to 15 of gestation. A control group was concurrently administered corn oil only, and an additional positive control group was administered 200 mg/kg of ethylene glycol monoethyl ether (EGEE) on days 10 to 12 of gestation.

Dose-related signs of clinical toxicity were observed in the treatment groups, including rough hair coat, loose stool, and urine-staining. Overall pregnancy weight gain was reduced in the 125.5 mg/kg group compared to the vehicle controls. Food consumption was not altered in any treatment group, nor were there differences in fertility, number of implantations, prenatal mortality, litter size, or fetal weights or lengths when compared with vehicle controls. Gross skeletal and visceral malformations were observed in the groups administered TCMTB, but the incidences were not dose-related or statistically significant compared to vehicle controls. TCMTB was concluded to be neither fetotoxic nor teratogenic, even at doses causing overt maternal toxicity in pregnant rats.

In a two generation reproduction study (105), male and female rats were randomised into 4 treatment groups of 24 males and 24 females each. The animals received diets containing 0, 25, 100, or 400 ppm TCMTB by weight. The parental (F_0) animals received treated diets for 68 days prior to pairing for

mating, then continued to receive TCMTB throughout one breeding cycle until termination after weaning of their first (F_1) litters. F_1 animals were randomly selected from each litter and weaned onto the same dietary concentrations of test material that their respective parents received. These animals were paired for mating at about 15 weeks of age and 2 successive breeding cycles were completed. The study was terminated after weaning of the second (F_2) litters.

There was no effect on either F_0 or F_1 animals in terms of clinically observed signs of toxicity, body weight, food consumption, fertility, or reproductive performance. A minor deficit in F_2 pup body weight development during lactation in the high dose group was observed; the animals weighed approximately 10% less than controls at weaning. The NOEL for TCMTB in the diet was set at 100 ppm (5.7-16.8 mg/kg/day).

10.0 OCCUPATIONAL EXPOSURE

One industrial hygiene survey was located (76). Results show that dermal contact with treated wood presents a greater exposure concern than inhalation of TCMTB. Workers at two BC sawmills using a water-based TCMTB formulation reported on-going problems with skin rashes, inflammation, or burns. In addition, workers reported occasional incidents of eye, nose, and throat irritation, chest tightness, and nosebleeds.

In the study, all monitored air levels of TCMTB were relatively low (<0.01 ppm), with the highest levels found in a grading area and in mixing rooms. Air levels of the contaminants CMTC and methyl isothiocyanate (MITC) were undetectable at all monitored sites. The by-product hydrogen cyanide was less than 0.1 ppm in the mixing rooms.

The grader and puller job categories showed the highest degree of hand contamination, but the glove performance (tearing, permeability) was inconsistent. The highest levels of TCMTB on cotton shirts were found in the chain puller job categories. The use of protective clothing was recommended to decrease skin contact with these compounds. Potential dermal exposure to CMTC, MITC, and hydrogen cyanide was not monitored.

Some information on the occupational impacts of TCMTB based on local experiences has also been reported (18). Complaints include occasional extreme skin sensitization to Busan 1030, occasional skin irritation, dryness of eyes, nose, and throat, and complaints of unpleasant odour.

BC Research (16) has cited several other occupational experiences with TCMTB. At one leather tanning company where TCMTB had been used continuously for 20 years, workers prepared formulations wearing rubber gloves, aprons, and boots, but not respirators. While some workers handling wet, treated leather developed mild skin irritation, no cases of eye, nose, or throat irritation or allergic dermatitis were reported. Similar experiences were reported at a tissue

paper plant in Wisconsin. However, one employee received mild skin burns when splashed with concentrated Busan 30.

Information from Finland (77) indicated that in five years of use, five cases of allergic contact dermatitis have been reported. A cross-sensitivity reaction with 2-MBT was a noted contributing factor. According to one survey, workers in Finland complained of irritation of the upper respiratory tract and headache, but not of nosebleeds.

Buckman Laboratories (78) reports that eye, throat, and other irritations may be caused by some minor impurities in TCMTB. CMTC, produced during the manufacturing process, is thought to be the chemical responsible for these effects (78).

An Acceptable Daily Intake (ADI), defined as the amount of a chemical to which humans can be exposed on a daily basis over an extended period of time without suffering a deleterious effect, has been established for TCMTB by the USEPA. This value is 0.025 mg/kg/day for oral exposure (79). The BC Ministry of Environment has also established an ADI of 0.014 mg/kg/day, or 1 mg/day for a 70 kg person (82); calculations are summarized in Appendix E.

11.0 FOOD USE

The currently registered uses of TCMTB do not permit the use of treated wood in situations where it is likely to come in direct contact with food products (22). The use of paper products produced from TCMTB treated wood or from pulp and paper mill processes in which TCMTB may be employed for food packaging applications is limited. Although the potential for dietary exposure to TCMTB as a result of such use is considered insignificant, the use of wood shavings as bedding or as a filler in feed for livestock may result in residues in animal tissues (22). Presently, there are insufficient data on these uses to permit comment on health and safety aspects of these practices.

12.0 ANALYTICAL METHODS OF DETECTION

Several references for the chemical detection of TCMTB were located. In 1985, BC Research (28) used a method developed by Forintek (93) to analyze TCMTB in aqueous solution. Samples containing TCMTB were diluted with acetonitrile, centrifuged, then analyzed on a high pressure liquid chromatograph (HPLC) equipped with a variable wavelength detector operating at 280 nm. A ten minute linear gradient program from 40% to 90% acetonitrile was used, and the results were compared with those from chromatography of a standard solution of TCMTB. Alternately, it was suggested that TCMTB be extracted with three aliquots of diethyl ether, and the ether extract diluted with acetonitrile before chromatography. The response was linear between 0.05 and 3.00 ug.

A more recent method developed by BC Research uses reverse phase HPLC (12). Samples are screened for high levels of TCMTB by direct injection; samples containing low levels of TCMTB are first extracted with methylene chloride, then analyzed. The raw extract may first be purified by Florisil column chromatography prior to analysis. The detection limits by direct injection and extraction are 20 ug/L and 1 ug/L, respectively.

Environment Canada uses a similar method for analysis of TCMTB and associated benzothiazoles in effluents and sediments (97). Detection limits for TCMTB, BT, 2-MBT, and MTBT in effluents are 1, 10, 25, and 5 ug/L, respectively. These detection limits are below those required to enforce provincial legislation for TCMTB in effluents (see below). Sediment detection limits are currently under evaluation.

The United States Environmental Protection Agency has developed a standard procedure (80) for analyzing TCMTB in industrial and municipal wastewaters, which is similar to that described above. TCMTB is extracted from water using methylene chloride, cleaned up on a deactivated silica gel column, and subjected to HPLC, eluting with a mixture of hexane, methanol, and methylene chloride. Detection limits are about 10 ug/L

The Workers' Compensation Board of British Columbia has established a protocol for analyzing TCMTB in air (81). TCMTB is collected by drawing a measured volume of air through a Teflon membrane filter, which is stored in a solution of phosphoric acid in methanol. The stored filter is sonicated and the solution is diluted with water. An aliquot of the extract is injected into a liquid chromatograph equipped with a UV photometric detector, and the sample is then quantified by comparing the peak area of the sample to that of standards. The range of detection is 0.1-120 ug TCMTB per sample, or approximately 0.001 to 1 mg/m^3 for a 120 L air sample.

Buckman Laboratories provided an HPLC method for analysis of TCMTB in liquids and solids (95). It involves extraction of samples with methylene chloride, then drying with anhydrous sodium sulphate. Sample calculations were provided, but detection limits were not.

In environmental fate studies (32), soil extracts were analyzed by extracting with methylene chloride then subjecting samples to HPLC. Further details of analysis were not provided.

13.0 EXISTING LEGISLATION

Existing provincial legislation (48) states that, from September 1, 1990 until September 1, 1991, the concentration of TCMTB in effluent shall not exceed 15 ug/L, based on the lowest recorded 96 hour LC50 for fish species (55). From September 1, 1991, concentration of TCMTB in effluent shall not exceed 6 ug/L.

The rate of emissions to the air from an antisapstain chemical spray booth stack cannot legally exceed 7.0 mg/second TCMTB, as determined by "approved" sampling and analytical methods. Derivation of an air emission recommendation is included in Appendix F.

14.0 CONCLUSION

A comparison of this paper with the previous version (83) shows that several important data gaps have been eliminated. For example, the physical and chemical properties of TCMTB and associated products have been more clearly established, the environmental fate of the chemical has been studied in further detail, and several toxicological studies have been done, including a comparison of toxicity of TCMTB to fish under freshwater and saltwater conditions. Carcinogenicity, teratogenicity, and feeding studies have been carried out by the manufacturer, eliminating some questions on chronic exposure effects, and impacts of the chemical on human health have been more clearly documented, owing mainly to an occupational exposure study. Analytical methods of detection in air, water, and soil have also been refined or established.

Although much progress has been made in filling toxicological data gaps, two important questions still remain. The environmental effects of TCMTB degradation products is perhaps most important. Such products have been tentatively or conclusively identified, but their environmental and toxicological impacts generally have not.

The second area of concern is that of chronic exposure of fish and other wildlife to TCMTB and its breakdown products. Testing of fish under saltwater and freshwater conditions may yield some answers, but long-term studies should be carried out.

It should be noted in closing that, although TCMTB appears to be more threatening to some forms of wildlife than do other antisapstain chemicals, the total environmental impact and toxicological effects of these chemicals must be considered and compared when deciding which should be allowed registration and use.

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Table 1: Comparison of toxicity values for "active" antisapstain chemicals and formulations

	Oral LD50* Rat - mg/kg	Dermal LD50* Rabbit - mg/kg	Aquatic 96hrLC50 Fish species**-ppm
NP-1	400[84]	1404[84]	0.49[84]
DDAC	84[85]	>1600[85]	0.55[85] Bluegills 0.27[85]
IPBC	1470[118]	>2000[118]	0.067[119]
TCMTB	750[26] (80% form)	>2000[52] (80% form)	0.039[64] Chinook Salmon 0.015[55]
2-MBT	500[111]	>5010[111]	0.73[111]***
Busan 1030	1200[22]	1080[57]	0.117[63] Chinook Salmon 0.055[22]
Copper-8	3900-4700[87] (18% susp.)	>2,000[87]	0.00016[87]
Ecobrite III	>5,000[94]	>2,000[94]	10-50[94]
NaT_4CP	210[96]	270[96]	0.3-0.13[96]
NaPCP	71[88]	250[89]	0.048[90] Coho Salmon 0.032[92]
PCP	27[89]	39[88]	0.044[91] Bluegills 0.020[91]

*Values quoted are the lowest published for each species.

**Fish species is Rainbow trout unless otherwise noted.

***2-MBT is not used as an antisapstain chemical, but is included here for toxicity comparison of a breakdown product and the parent compound.

APPENDIX A

INFORMATION SOURCES SEARCHED FOR CITATIONS ON TCMTB

A number of databases were searched for citations on TCMTB, Busan, 2-(thiocyanomethylthio)benzothiazole, and 21564-17-0, the CAS Registry Number for TCMTB:

Toxline
Toxback
CCOHS Trade Names, Cheminfo, Nioshtic, and Ciseng
Biosis Previews
Excerpta Medica
International Pharmaceutical Abstracts
Life Sciences Collection
Chemical Exposure
Chemical Regulations and Guidelines System
Drug Information Fulltext
CA Search
NTIS
Medline
Clinical Abstracts
SCISEARCH
Enviroline
Pollution Abstracts
Environmental Bibliography
Chemname
Chem Business Newsbase
Compendex
Agricola
Oceanic Abstracts

APPENDIX B

MAMMALIAN LETHAL TOXICITY CLASSES FOR CHEMICAL COMPOUNDS*

Toxicity Rating	Commonly Used Term	Oral/Dermal** (mg/kg)	Inhalation‡ (ppm-mg/L)
1	Practically Nontoxic	>15,000	>200
2	Slightly Toxic	5,000-15,000	20-200
3	Moderately Toxic	500-5,000	2-20
4	Very Toxic	50-500	0.2-2
5	Extremely Toxic	5-50	0.02-0.2
6	Ultra Toxic	<5	<0.02

*Toxicity ratings adapted from references 54, 113, and 115.

**Index: acute oral or dermal LD50.

‡Index: LC50 - four hour inhalation exposure.

APPENDIX C

AQUATIC LETHAL TOXICITY CLASSES FOR CHEMICAL COMPOUNDS*

Toxicity Rating	Commonly Used Term	Exposure Conc.** (ppm - mg/L)
1	Practically Nontoxic	>100
2	Slightly Toxic	10-100
3	Moderately Toxic	1-10
4	Very Toxic	0.1-1
5	Extremely Toxic	0.01-0.1
6	Ultra Toxic	<0.01

*Toxicity ratings adapted in consultation with reference 103.

**Index: 96 hour LC50 or EC50.

APPENDIX D

Derivation of Stormwater Effluent Criteria for TCMTB

Adapting a method used by Fox for other antisapstain chemicals (see Reference 107 for more details), the formula for calculation of a stormwater discharge criteria is as follows:

Criteria = 96 hour LC50 x AF x EF x DMF x DF

where:
- AF = acute toxicity safety factor (1.0)
- EF = environmental fate safety factor (1.0)
- DMF = degradation product and metabolite hazards safety factor (1.0)
- DF = dilution factor (1.0)

The 96 hour LC50 used is the value for the most sensitive salmonid species, i.e. Chinook salmon. This value is 15 ppb for pure TCMTB (55), the value used in antisapstain stormwater effluent legislation (48).

APPENDIX E

Calculating an Acceptable Daily Intake (ADI) for Humans

Following methods used by Ward and the USEPA (82, 108), an ADI for TCMTB may be derived for humans based on the 20 mg/kg/day intake by rats in the 104 week dietary carcinogenicity study (26):

Calculation of human ADI based on rat NOEL

a) Safety factor used: 100x

i.e., 10x for conversion of animal to human data (interspecies variability)
10x for human biological variation (intraspecies variability)

b) Human TCMTB ADI: = 20 mg/kg/day/100
= 0.20 mg/kg/day

c) For a 70 kg adult human: = 0.20 mg/kg/day x 70 kg
= 14 mg/day ADI

For a 17 kg child: = 0.20 mg/kg/day x 17 kg
= 3.4 mg/day ADI

APPENDIX F

Calculation of an Air Emission Guideline for TCMTB

Based on the ADI given in Appendix E, an emission guideline is calculated below. A method used by Ward (82) is followed.

I. Assumptions

Adult
daily respiration = a) 20 m^3* or b) 24.8 m^3**
mean body weight = 70 kg
absorbs 100% of inhaled TCMTB
respiration is only route of exposure

*This respiration value is based on values from the US Environmental Protection Agency (56).

**This respiration value is based on the sum of two respiratory rates over 24 hours: a "moderate activity" rate of 2.1 m^3/hour, over an 8-hour work shift, and a "light activity" rate of 0.5 m^3/hour, over 16 hours (118). The "light activity" rate is included as a conservative factor which assumes the exposure of mill workers to antisapstain chemicals off-site through such routes as contaminated workclothes.

II. Conversion of TCMTB ADI to ug/m^3/day

Adult ADI_{70}

a) 14 mg/day = 14 mg/20 m^3/day
= 0.7 mg/m^3/day
= 700 ug/m^3/day

b) 14 mg/day = 14mg/24.8 m^3/day
= 0.56 mg/m^3/day
= 560 ug/m^3/day (24 hour ambient air guideline)

III. Conversion of 24 hour ambient air guideline to 1 hour ambient air guideline

For use in subsequent dispersion modelling calculations, the 24 hour ambient air guideline should be converted to a 1 hour ambient air guideline. The more conservative value of 560 ug/m^3/day is used in this calculation. Using the formula (110):

$$C2 = C1 \times (T1/T2)^a$$

where C2 = 1 hour average concentration
C1 = concentration at time T1
T1 = time period of the original standard
T2 = 1 hour
a = exponent = 0.28

then the one hour ambient air guideline is as follows:

$$560 \times (24/1)^{0.28} = 1363 \text{ ug/m}^3$$

The recommended interim ambient one hour guideline for TCMTB is 1360 ug/m^3.

IV. Calculation of an Emission Guideline through Dispersion Modelling

Given meteorology data and stack characteristics (112), an emission rate of 5200 g TCMTB/sec would give a maximum ground level concentration of 1 g/m^3. For a maximum ground concentration of 1360 ug/m^3 to arise, an emission rate of 7.07 g/sec would be required:

$$5200 \text{ m}^3/\text{sec} \times 1.36 \times 10^{-3} \text{ g/m}^3 = 7.07 \text{ g/sec.}$$

Using an engineering safety factor of 35, as used to develop an emission guideline for chlorophenates (111), an appropriate guideline for TCMTB is as follows:

$$7.07/35 = 2.0 \times 10^{-1} \text{ g/sec}$$
$$= 200 \text{ mg/sec}$$

N.B. Existing provincial legislation (48) allows TCMTB spray booth emissions of 7.0 mg/second, based on capabilities of available technology.

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